

Pentaerythritol derivatives and a method for preparation thereof, and liquid crystal base containing the same

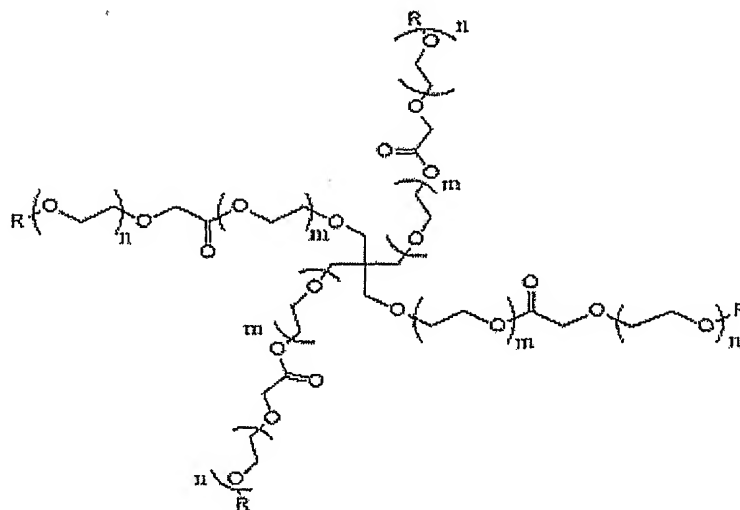
BACKGROUND OF THE INVENTION

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1. Field of the Invention

The present invention relates to pentaerythritol derivatives represented by the following formula 1, which improve the moisture retaining ability of the stratum corneum when applied to the skin, and especially show high moisturizing ability even in dry conditions, to a preparation method thereof, and to a liquid crystal base containing the same.

[Formula 1]



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(Wherein R is the same or different, saturated or unsaturated, linear or branched alkyl groups of 1 to 24 carbon atoms having hydrogen or hydroxy

group or not; m and n are the same or different integers of which m is 0 to 10 and n is 1 to 10).

2. Description of Prior Art

5 The stratum corneum of the skin has the functions of protecting the human body from external harmful substances, and preventing moisture inside the skin from evaporating outside, thereby maintaining skin moistness. However, as the skin becomes aged, these functions of the stratum corneum deteriorate and the skin becomes easily dry. Moreover this tendency is increased in dry winter
10 conditions.

 Therefore, in order to improve skin dryness, numerous moisturizers have been developed. Representative examples are water-soluble moisturizers and ceramides. Because water-soluble moisturizers such as amino acid, organic acid and urea have excellent water absorbing ability, and provide moisture for the
15 stratum corneum layer, they are used as general moisturizers. However, they show the problem that moisturizing ability decreases drastically in dry conditions of low humidity such as in winter. Further, although ceramides, as important constituents of intercellular lipid in the stratum corneum cells, have an excellent effect on enhancing skin barrier function and maintaining skin moisture, their
20 stability of formulation decreases when used in high content because they have low compatibility with oils used in cosmetic compositions. Therefore, ceramides have been difficult to use in substantially effective concentration.

Therefore, there is a need to develop oil-soluble moisturizers that have high moisturizing ability, thus having an excellent effect on moisture maintenance even in dry conditions, and also being easy to use in cosmetic compositions.

The present inventors have studied to develop oil-soluble moisturizers, and
5 as a result, have developed pentaerythritol derivatives represented by the following formula 1, which show high moisturizing ability even in dry conditions, to complete the present invention.

SUMMARY OF THE INVENTION

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An object of the present invention is to provide pentaerythritol derivatives represented by the following formula 1, which improve the moisture retaining ability of the stratum corneum when applied to the skin, and especially show high moisturizing ability even in dry conditions.

15 Another object of the present invention is to provide a method for preparing the above-mentioned pentaerythritol derivatives.

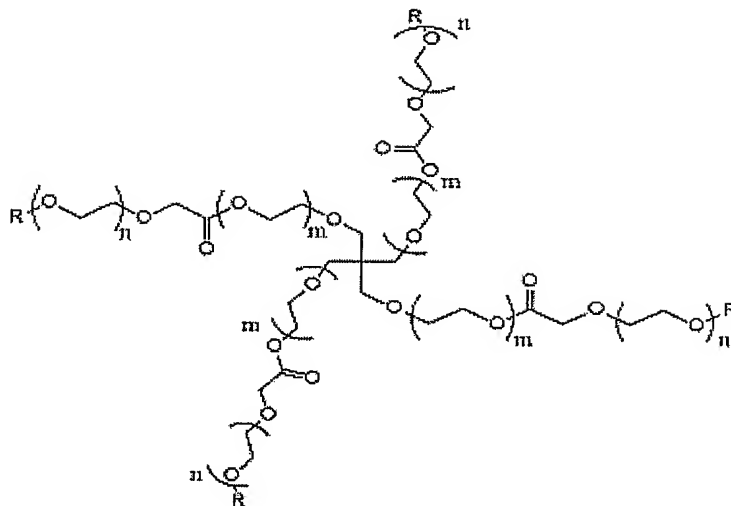
A further object of the present invention is to provide a liquid crystal base containing above-mentioned pentaerythritol derivatives.

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DETAILED DESCRIPTION OF THE INVENTION

According to the present invention, pentaerythritol derivatives represented by the following formula 1 are provided:

[Formula 1]



(Wherein R is the same or different, saturated or unsaturated, linear or branched alkyl groups of 1 to 24 carbon atoms having hydrogen or hydroxy group or not; m and n are the same or different integers of which m is 0 to 10 and n is 1 to 10).

The pentaerythritol derivatives according to the present invention, as is confirmed by the Examples below, improve the water maintenance ability of the stratum corneum when applied to the skin, and especially show high moisturizing ability even in dry conditions. Further, the pentaerythritol derivatives of the invention may be combined in high content into a liquid crystal base, thereby stably forming liquid crystal.

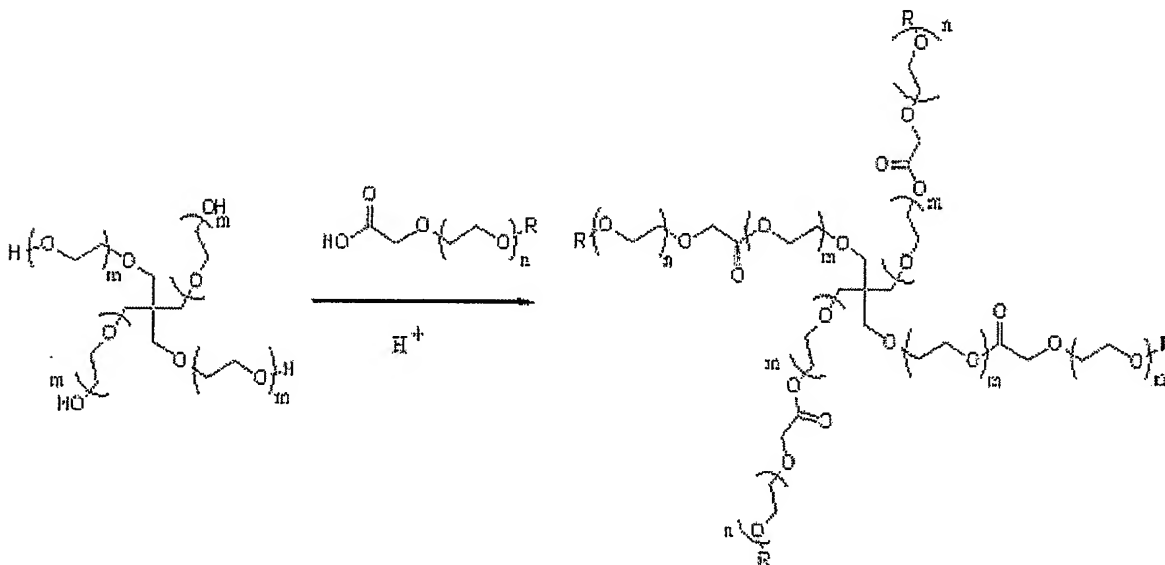
The pentaerythritol derivatives according to the invention may be prepared by a method comprising the steps of:

(1) Synthesizing pentaerythritol derivatives by refluxing pentaerythritol, pentaerythritol ethoxylate or pentaerythritol propoxylate with carboxylic acid having ethylene glycol repeat unit (-OCH₂CH₂O-), in the presence of acid catalyst;

5 (2) Purifying the pentaerythritol derivatives prepared in step (1).

A method for preparing pentaerythritol derivatives according to the present invention may be schematized by the following reaction scheme:

[Reaction scheme 1]



10 Hereinafter, a method for preparing pentaerythritol derivatives according to the present invention is described in detail.

Step (1): Synthesis of pentaerythritol derivatives

As the pentaerythritol ethoxylate or pentaerythritol propoxylate in step (1),
 15 pentaerythritol ethoxylate or pentaerythritol propoxylate having 4 to 40 ethylene

glycol repeat units (-OCH₂CH₂O-) or propylene glycol repeat units (-OCH₂CH₂CH₂O-) in its molecule may be employed.

In addition, as the carboxylic acid in step (1), saturated or unsaturated, linear or branched carboxylic acid of 6 to 75 carbon atoms may be employed. For example, glycolic acid ethoxylate 4-*tert*-butylphenyl ether, glycolic acid ethoxylate 4-nonylphenyl ether, glycolic acid ethoxylate hexyl ether, glycolic acid ethoxylate heptyl ether, glycolic acid ethoxylate octyl ether, glycolic acid ethoxylate nonyl ether, glycolic acid ethoxylate decyl ether, glycolic acid ethoxylate lauryl ether, glycolic acid ethoxylate tetradecyl ether, glycolic acid ethoxylate hexadecyl ether, glycolic acid ethoxylate stearyl ether or glycolic acid ethoxylate oleyl ether, which should not be considered to limit the scope of the present invention, may be employed.

As an organic solvent in step (1), solvent which is azeotropic distillable with water is preferred, for example, benzene, toluene, xylene, or the like may be employed. Also, the mixed solvent of these solvents with dichloromethane, tetrahydrofuran, acetic acid ethyl, acetonitrile, chloroform, ethyl ether, trichloroethylene, dimethylformamide, or the like may be used. Further, solvent-free reaction in which organic solvent is not used is also possible.

In addition, as an acid catalyst in step (1), organic acid such as p-toluene sulfonic acid, pyridine p-toluene sulfonic acid salt or the like; or inorganic acid such as sulfuric acid, hydrochloric acid or the like may be employed. Usage equivalents may be 0.001 ~ 2, and preferably 0.01 ~ 2, because reaction slows down below 0.01, and side reaction may occur above 2.

Step (2): Purification of pentaerythritol derivatives

The pentaerythritol derivatives synthesized in step (1) may be purified by aliquoting with nonpolar solvent to remove impurities.

5 As nonpolar solvent in this step, examples are pentane, hexane, heptane, cyclohexane, octane, isooctane, decane, and the like, which should not be considered to limit the scope of the present invention. Usage amount of nonpolar solvent may be 30~200% based on the mass of pentaerythritol derivatives, and preferably 70~150%, because removing impurities is not easy below 70%,
10 and the yield may be decreased above 150%.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the liquid crystal base of Preparation Example 3 observed
15 by polarizing microscope.

Figure 2 shows the liquid crystal base of Preparation Example 8 observed by polarizing microscope.

Figure 3 shows the liquid crystal base of Preparation Example 17 observed by polarizing microscope.

20 Figure 4 shows the liquid crystal base of Preparation Example 21 observed by polarizing microscope.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will be described in more detail by way of the following examples. However, these examples are provided for the purpose of illustration only and should not be construed as limiting the scope of the invention, which will be apparent to one skilled in the art.

<Example 1> Preparation of pentaerythritol glycolic ester ethoxylate hexyl ether (pentaerythritol hexeth-4 carboxylate)

13.6 g (100 mmol) of pentaerythritol and 110.4 g (400 mmol) of glycolic ethoxylate hexyl ether(hexeth-4 carboxylic acid) were dissolved in 2ℓ of benzene. To the resultant solution, 7.6 g (40 mmol) of p-toluene sulponic acid was added and refluxed while stirring. Eliminating water with Dean-stark, the reaction was continued for 8 hours.

After the reaction was complete, the organic layer was washed twice with 1ℓ of water, dried with anhydrous sodium sulfate and then filtrated. After filtration, the remaining solution was distilled under reduced pressure, concentrated, and aliquoted with 100 mℓ of hexane to remove the hexane layer. The remaining aliquot was again distilled under reduced pressure and concentrated to obtain 93 g of pentaerythritol glycolic ester ethoxylate hexyl ether (pentaerythritol hexeth-4 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.18(16H), 3.65(48H), 3.44(8H, t, $J=6.9\text{Hz}$), 1.57(8H, m), 1.26(24H), 0.88(12H, t, $J=6.6\text{Hz}$)

<Example 2> Preparation of pentaerythritol glycolic ester ethoxylate hexyl ether
(pentaerythritol hexeth-6 carboxylate)

Except that 145.6 g (400 mmol) of glycolic ethoxylate hexyl ether
5 (hexeth-6 carboxylic acid) was used instead of glycolic ethoxylate hexyl ether
(hexeth-4 carboxylic acid), the same procedure described in Example 1 was
performed to obtain 121.5 g of pentaerythritol glycolic ester ethoxylate hexyl
ether (pentaerythritol hexeth-6 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.18(16H), 3.66(80H), 3.44(8H, t, $J=6.9\text{Hz}$),
10 1.56(8H, m), 1.26(24H), 0.88(12H, t, $J=6.6\text{Hz}$)

<Example 3> Preparation of pentaerythritol glycolic ester ethoxylate octyl ether
(pentaerythritol capreth-4 carboxylate)

Except that 121.6 g (400 mmol) of glycolic ethoxylate octyl ether (capreth-4
15 carboxylic acid) was used instead of glycolic ethoxylate hexyl ether (hexeth-4
carboxylic acid), the same procedure described in Example 1 was performed to
obtain 104.6 g of pentaerythritol glycolic ester ethoxylate octyl ether
(pentaerythritol capreth-4 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.17(16H), 3.66(48H), 3.45(8H, t, $J=6.9\text{Hz}$),
20 1.57(8H, m), 1.26(40H), 0.88(12H, t, $J=6.6\text{Hz}$)

<Example 4> Preparation of pentaerythritol glycolic ester ethoxylate octyl ether (pentaerythritol capreth-6 carboxylate)

Except that 164.0 g (400 mmol) of glycolic ethoxylate octyl ether (capreth-6 carboxylic acid) was used instead of glycolic ethoxylate hexyl ether (hexeth-4 carboxylic acid), the same procedure described in Example 1 was performed to obtain 137.2 g of pentaerythritol glycolic ester ethoxylate octyl ether (pentaerythritol capreth-6 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.17(16H), 3.66(80H), 3.46(8H, t, $J=6.9\text{Hz}$), 1.57(8H, m), 1.26(40H), 0.87(12H, t, $J=6.6\text{Hz}$)

<Example 5> Preparation of pentaerythritol glycolic ester ethoxylate lauryl ether (pentaerythritol laureth-4 carboxylate)

Except that 144.0 g (400 mmol) of glycolic ethoxylate lauryl ether (laureth-4 carboxylic acid) was used instead of glycolic ethoxylate hexyl ether (hexeth-4 carboxylic acid), the same procedure described in Example 1 was performed to obtain 121.2 g of pentaerythritol glycolic ester ethoxylate lauryl ether (pentaerythritol laureth-4 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.17(16H), 3.66(48H), 3.46(8H, t, $J=6.9\text{Hz}$), 1.57(8H, m), 1.26(72H), 0.88(12H, t, $J=6.6\text{Hz}$)

<Example 6> Preparation of pentaerythritol glycolic ester ethoxylate lauryl ether (pentaerythritol laureth-6 carboxylate)

Except that 184.0 g (400 mmol) of glycolic ethoxylate lauryl ether (laureth-6 carboxylic acid) was used instead of glycolic ethoxylate hexyl ether (hexeth-4 carboxylic acid), the same procedure described in Example 1 was performed to obtain 158.5 g of pentaerythritol glycolic ester ethoxylate lauryl ether (pentaerythritol laureth-6 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.17(16H), 3.66(80H), 3.47(8H, t, $J=6.9\text{Hz}$), 1.57(8H, m), 1.26(72H), 0.88(12H, t, $J=6.6\text{Hz}$)

<Example 7> Preparation of pentaerythritol glycolic ester ethoxylate lauryl ether (pentaerythritol laureth-10 carboxylate)

Except that 254.4 g (400 mmol) of glycolic ethoxylate lauryl ether (laureth-10 carboxylic acid) was used instead of glycolic ethoxylate hexyl ether (hexeth-4 carboxylic acid), the same procedure described in Example 1 was performed to obtain 218.4 g of pentaerythritol glycolic ester ethoxylate lauryl ether (pentaerythritol laureth-10 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.17(16H), 3.67(144H), 3.46(8H, t, $J=6.9\text{Hz}$), 1.57(8H, m), 1.27(72H), 0.88(12H, t, $J=6.6\text{Hz}$)

<Example 8> Preparation of pentaerythritol glycolic ester ethoxylate cetyl ether (pentaerythritol ceteth-4 carboxylate)

Except that 162.4 g (400 mmol) of glycolic ethoxylate cetyl ether (ceteth-4 carboxylic acid) was used instead of glycolic ethoxylate hexyl ether (hexeth-4 carboxylic acid), the same procedure described in Example 1 was performed to

obtain 138.2 g of pentaerythritol glycolic ester ethoxylate cetyl ether (pentaerythritol ceteth-4 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.17(16H), 3.67(48H), 3.46(8H, t, $J=6.9\text{Hz}$), 1.57(8H, m), 1.26(104H), 0.88(12H, t, $J=6.6\text{Hz}$)

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<Example 9> Preparation of pentaerythritol glycolic ester ethoxylate cetyl ether (pentaerythritol ceteth-6 carboxylate)

Except that 197.6 g (400 mmol) of glycolic ethoxylate cetyl ether (ceteth-6 carboxylic acid) was used instead of glycolic ethoxylate hexyl ether (hexeth-4
10 carboxylic acid), the same procedure described in Example 1 was performed to obtain 163.8 g of pentaerythritol glycolic ester ethoxylate cetyl ether (pentaerythritol ceteth-6 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.17(16H), 3.67(80H), 3.47(8H, t, $J=6.9\text{Hz}$), 1.57(8H, m), 1.26(104H), 0.87(12H, t, $J=6.6\text{Hz}$)

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<Example 10> Preparation of pentaerythritol glycolic ester ethoxylate cetyl ether (pentaerythritol ceteth-10 carboxylate)

Except that 268.0 g (400 mmol) of glycolic ethoxylate cetyl ether (ceteth-10 carboxylic acid) was used instead of glycolic ethoxylate hexyl ether (hexeth-4
20 carboxylic acid), the same procedure described in Example 1 was performed to obtain 247.4 g of pentaerythritol glycolic ester ethoxylate cetyl ether (pentaerythritol ceteth-10 carboxylate).

^1H -NMR (in CHCl_3): 4.17(16H), 3.67(144H), 3.47(8H, t, $J=6.9\text{Hz}$), 1.57(8H, m), 1.26(104H), 0.87(12H, t, $J=6.6\text{Hz}$)

<Example 11> Preparation of pentaerythritol glycolic ester ethoxylate oleyl ether (pentaerythritol oleth-6 carboxylate)

Except that 216.0 g (400 mmol) of glycolic ethoxylate oleyl ether (oleth-6 carboxylic acid) was used instead of glycolic ethoxylate hexyl ether (hexeth-4 carboxylic acid), the same procedure described in Example 1 was performed to obtain 187.1 g of pentaerythritol glycolic ester ethoxylate oleyl ether (pentaerythritol oleth-6 carboxylate).

^1H -NMR (in CHCl_3): 5.64(8H), 4.16(16H), 3.67(80H), 3.47(8H, t, $J=6.9\text{Hz}$), 2.02(16H), 1.57(8H, m), 1.27(80H), 0.87(12H, t, $J=6.6\text{Hz}$)

<Example 12> Preparation of pentaerythritol glycolic ester ethoxylate stearyl ether (pentaerythritol steareth-4 carboxylate)

Except that 173.6 g (400 mmol) of glycolic ethoxylate stearyl ether (steareth-4 carboxylic acid) was used instead of glycolic ethoxylate hexyl ether (hexeth-4 carboxylic acid), the same procedure described in Example 1 was performed to obtain 151.1 g of pentaerythritol glycolic ester ethoxylate stearyl ether (pentaerythritol steareth-4 carboxylate).

^1H -NMR (in CHCl_3): 4.17(16H), 3.68(48H), 3.47(8H, t, $J=6.9\text{Hz}$), 1.57(8H, m), 1.26(120H), 0.88(12H, t, $J=6.6\text{Hz}$)

<Example 13> Preparation of pentaerythritol glycolic ester ethoxylate stearyl ether (pentaerythritol steareth-6 carboxylate)

Except that 208.8 g (400 mmol) of glycolic ethoxylate stearyl ether (steareth-6 carboxylic acid) was used instead of glycolic ethoxylate hexyl ether (hexeth-4 carboxylic acid), the same procedure described in Example 1 was performed to obtain 183.6 g of pentaerythritol glycolic ester ethoxylate stearyl ether (pentaerythritol steareth-6 carboxylate).

¹H-NMR (in CHCl₃): 4.17(16H), 3.67(80H), 3.47(8H, t, J=6.6Hz), 1.57(8H, m), 1.26(120H), 0.87(12H, t, J=6.6Hz)

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<Example 14> Preparation of pentaerythritol glycolic ester ethoxylate stearyl ether (pentaerythritol steareth-10 carboxylate)

Except that 279.2 g (400 mmol) of glycolic ethoxylate stearyl ether (steareth-10 carboxylic acid) was used instead of glycolic ethoxylate hexyl ether (hexeth-4 carboxylic acid), the same procedure described in Example 1 was performed to obtain 238.1 g of pentaerythritol glycolic ester ethoxylate stearyl ether (pentaerythritol steareth-10 carboxylate).

¹H-NMR (in CHCl₃): 4.17(16H), 3.67(144H), 3.47(8H, t, J=6.9Hz), 1.58(8H, m), 1.26(120H), 0.88(12H, t, J=6.6Hz)

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<Example 15> Preparation of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate hexyl ether (pentaerythritol ethoxylate (3/4 EO/OH) hexeth-4 carboxylate)

Except that 27.0 g (100 mmol) of pentaerythritol ethoxylate (3/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 1 was performed to obtain 136.5 g of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate hexyl ether (pentaerythritol ethoxylate (3/4 EO/OH) hexeth-4 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.17(16H), 3.67(60H), 3.44(8H, t, $J=6.9\text{Hz}$), 1.56(8H, m), 1.26(24H), 0.88(12H, t, $J=6.6\text{Hz}$)

<Example 16> Preparation of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate hexyl ether (pentaerythritol ethoxylate (3/4 EO/OH) hexeth-6 carboxylate)

Except that 27.0 g (100 mmol) of pentaerythritol ethoxylate (3/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 2 was performed to obtain 137.1 g of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate hexyl ether (pentaerythritol ethoxylate (3/4 EO/OH) hexeth-6 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.18(16H), 3.66(92H), 3.44(8H, t, $J=6.9\text{Hz}$), 1.57(8H, m), 1.26(24H), 0.88(12H, t, $J=6.6\text{Hz}$)

<Example 17> Preparation of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate octyl ether(pentaerythritol ethoxylate (3/4 EO/OH) capreth-4 carboxylate)

Except that 27.0 g (100 mmol) of pentaerythritol ethoxylate (3/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 3 was performed to obtain 119.9 g of pentaerythritol ethoxylate(3/4 EO/OH) glycolic ester ethoxylate octyl ether (pentaerythritol ethoxylate(3/4 EO/OH) capreth-4 carboxylate).

¹H-NMR (in CHCl₃): 4.17(16H), 3.66(60H), 3.45(8H, t, J=6.9Hz), 1.57(8H, m), 1.26(40H), 0.87(12H, t, J=6.6Hz)

<Example 18> Preparation of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate octyl ether (pentaerythritol ethoxylate (3/4 EO/OH) capreth-6 carboxylate)

Except that 27.0 g (100 mmol) of pentaerythritol ethoxylate (3/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 4 was performed to obtain 153.1 g of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate octyl ether (pentaerythritol ethoxylate (3/4 EO/OH) capreth-6 carboxylate).

¹H-NMR (in CHCl₃): 4.17(16H), 3.67(92H), 3.46(8H, t, J=6.9Hz), 1.57(8H, m), 1.26(40H), 0.88(12H, t, J=6.6Hz)

<Example 19> Preparation of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate lauryl ether (pentaerythritol ethoxylate (3/4 EO/OH) laureth-4 carboxylate)

Except that 27.0 g (100 mmol) of pentaerythritol ethoxylate (3/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 5 was performed to obtain 136.8 g of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate lauryl ether (pentaerythritol ethoxylate (3/4 EO/OH) laureth-4 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.17(16H), 3.66(60H), 3.47(8H, t, $J=6.9\text{Hz}$), 1.57(8H, m), 1.26(72H), 0.88(12H, t, $J=6.6\text{Hz}$)

<Example 20> Preparation of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate lauryl ether (pentaerythritol ethoxylate (3/4 EO/OH) laureth-6 carboxylate)

Except that 27.0 g (100 mmol) of pentaerythritol ethoxylate (3/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 6 was performed to obtain 164.2 g of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate lauryl ether (pentaerythritol ethoxylate (3/4 EO/OH) laureth-6 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.16(16H), 3.66(92H), 3.47(8H, t, $J=6.9\text{Hz}$), 1.57(8H, m), 1.26(72H), 0.89(12H, t, $J=6.6\text{Hz}$)

<Example 21> Preparation of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate lauryl ether (pentaerythritol ethoxylate (3/4 EO/OH) laureth-10 carboxylate)

Except that 27.0 g (100 mmol) of pentaerythritol ethoxylate (3/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 7 was performed to obtain 234.1 g of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate lauryl ether (pentaerythritol ethoxylate (3/4 EO/OH) laureth-10 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.17(16H), 3.67(156H), 3.47(8H, t, $J=6.9\text{Hz}$), 1.57(8H, m), 1.27(72H), 0.88(12H, t, $J=6.6\text{Hz}$)

<Example 22> Preparation of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate cetyl ether (pentaerythritol ethoxylate (3/4 EO/OH) ceteth-4 carboxylate)

Except that 27.0 g (100 mmol) of pentaerythritol ethoxylate (3/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 8 was performed to obtain 148.9 g of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate cetyl ether (pentaerythritol ethoxylate (3/4 EO/OH) ceteth-4 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.17(16H), 3.67(60H), 3.47(8H, t, $J=6.6\text{Hz}$), 1.57(8H, m), 1.27(104H), 0.88(12H, t, $J=6.6\text{Hz}$)

<Example 23> Preparation of pentaerythritol ethoxylate(3/4 EO/OH) glycolic ester ethoxylate cetyl ether(pentaerythritol ethoxylate(3/4 EO/OH) ceteth-6 carboxylate)

Except that 27.0 g (100 mmol) of pentaerythritol ethoxylate (3/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 9 was performed to obtain 174.8 g of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate cetyl ether (pentaerythritol ethoxylate (3/4 EO/OH) ceteth-6 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.17(16H), 3.67(92H), 3.47(8H, t, $J=6.9\text{Hz}$), 1.56(8H, m), 1.26(104H), 0.87(12H, t, $J=6.6\text{Hz}$)

<Example 24> Preparation of pentaerythritol ethoxylate 3/4 EO/OH) glycolic ester ethoxylate cetyl ether (pentaerythritol ethoxylate (3/4 EO/OH) ceteth-10 carboxylate)

Except that 27.0 g (100 mmol) of pentaerythritol ethoxylate (3/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 10 was performed to obtain 259.0 g of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate cetyl ether (pentaerythritol ethoxylate (3/4 EO/OH) ceteth-10 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.18(16H), 3.67(156H), 3.47(8H, t, $J=6.9\text{Hz}$), 1.57(8H, m), 1.26(104H), 0.87(12H, t, $J=6.6\text{Hz}$)

<Example 25> Preparation of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate oleyl ether (pentaerythritol ethoxylate (3/4 EO/OH) oleth-6 carboxylate)

Except that 27.0 g (100 mmol) of pentaerythritol ethoxylate (3/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 11 was performed to obtain 208.7 g of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate oleyl ether (pentaerythritol ethoxylate (3/4 EO/OH) oleth-6 carboxylate).

¹H-NMR (in CHCl₃): 5.64(8H), 4.17(16H), 3.67(92H), 3.47(8H, t, J=6.9Hz), 2.01(16H), 1.57(8H, m), 1.27(80H), 0.88(12H, t, J=6.6Hz)

<Example 26> Preparation of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate stearyl ether (pentaerythritol ethoxylate (3/4 EO/OH) steareth-4 carboxylate)

Except that 27.0 g (100 mmol) of pentaerythritol ethoxylate (3/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 12 was performed to obtain 159.1 g of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate stearyl ether (pentaerythritol ethoxylate (3/4 EO/OH) steareth-4 carboxylate).

¹H-NMR (in CHCl₃): 4.17(16H), 3.68(60H), 3.47(8H, t, J=6.9Hz), 1.57(8H, m), 1.27(120H), 0.87(12H, t, J=6.6Hz)

<Example 27> Preparation of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate stearyl ether (pentaerythritol ethoxylate (3/4 EO/OH) steareth-6 carboxylate)

Except that 27.0 g (100 mmol) of pentaerythritol ethoxylate (3/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 13 was performed to obtain 194.8 g of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate stearyl ether (pentaerythritol ethoxylate (3/4 EO/OH) steareth-6 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.17(16H), 3.67(92H), 3.47(8H, t, $J=6.6\text{Hz}$), 1.57(8H, m), 1.27(120H), 0.87 (12H, t, $J=6.6\text{Hz}$)

<Example 28> Preparation of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate stearyl ether (pentaerythritol ethoxylate (3/4 EO/OH) steareth-10 carboxylate)

Except that 27.0 g (100 mmol) of pentaerythritol ethoxylate (3/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 14 was performed to obtain 250.7 g of pentaerythritol ethoxylate (3/4 EO/OH) glycolic ester ethoxylate stearyl ether (pentaerythritol ethoxylate (3/4 EO/OH) steareth-10 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.17(16H), 3.67(156H), 3.47(8H, t, $J=6.9\text{Hz}$), 1.58(8H, m), 1.26(120H), 0.88(12H, t, $J=6.6\text{Hz}$)

<Example 29> Preparation of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate hexyl ether (pentaerythritol ethoxylate (15/4 EO/OH) hexeth-4 carboxylate)

Except that 79.7 g (100 mmol) of pentaerythritol ethoxylate (15/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 1 was performed to obtain 183.5 g of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate hexyl ether (pentaerythritol ethoxylate (15/4 EO/OH) hexeth-4 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.17(16H), 3.67(108H), 3.43(8H, t, $J=6.9\text{Hz}$), 1.56(8H, m), 1.26(24H), 0.88(12H, t, $J=6.6\text{Hz}$)

<Example 30> Preparation of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate hexyl ether (pentaerythritol ethoxylate (15/4 EO/OH) hexeth-6 carboxylate)

Except that 79.7 g (100 mmol) of pentaerythritol ethoxylate(15/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 2 was performed to obtain 187.1 g of pentaerythritol ethoxylate(15/4 EO/OH) glycolic ester ethoxylate hexyl ether(pentaerythritol ethoxylate(15/4 EO/OH) hexeth-6 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.18(16H), 3.66(140H), 3.44(8H, t, $J=6.9\text{Hz}$), 1.56(8H, m), 1.26(24H), 0.88(12H, t, $J=6.6\text{Hz}$)

<Example 31> Preparation of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate octyl ether (pentaerythritol ethoxylate (15/4 EO/OH) capreth-4 carboxylate)

Except that 79.7 g (100 mmol) of pentaerythritol ethoxylate (15/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 3 was performed to obtain 170.2 g of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate octyl ether (pentaerythritol ethoxylate (15/4 EO/OH) capreth-4 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.17(16H), 3.66(108H), 3.45(8H, t, $J=6.9\text{Hz}$), 1.57(8H, m), 1.26(40H), 0.88(12H, t, $J=6.6\text{Hz}$)

<Example 32> Preparation of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate octyl ether (pentaerythritol ethoxylate (15/4 EO/OH) capreth-6 carboxylate)

Except that 79.7 g (100 mmol) of pentaerythritol ethoxylate (15/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 4 was performed to obtain 201.1 g of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate octyl ether (pentaerythritol ethoxylate (15/4 EO/OH) capreth-6 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.17(16H), 3.67(140H), 3.47(8H, t, $J=6.9\text{Hz}$), 1.56(8H, m), 1.26(40H), 0.88(12H, t, $J=6.6\text{Hz}$)

<Example 33> Preparation of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate lauryl ether (pentaerythritol ethoxylate (15/4 EO/OH) laureth-4 carboxylate)

Except that 79.7 g (100 mmol) of pentaerythritol ethoxylate (15/4 EO/OH) was used instead of pentaerythritol, the same procedure in Example 5 was performed to obtain 188.8 g of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate lauryl ether (pentaerythritol ethoxylate (15/4 EO/OH) laureth-4 carboxylate).

¹H-NMR (in CHCl₃): 4.16(16H), 3.66(108H), 3.47(8H, t, J=6.9Hz), 1.57(8H, m), 1.26(72H), 0.88(12H, t, J=6.6Hz)

<Example 34> Preparation of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate lauryl ether (pentaerythritol ethoxylate (15/4 EO/OH) laureth-6 carboxylate)

Except that 79.7 g (100 mmol) of pentaerythritol ethoxylate (15/4 EO/OH) was used instead of pentaerythritol, the same procedure in Example 6 was performed to obtain 213.7 g of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate lauryl ether (pentaerythritol ethoxylate (15/4 EO/OH) laureth-6 carboxylate).

¹H-NMR (in CHCl₃): 4.16(16H), 3.66(140H), 3.46(8H, t, J=6.9Hz), 1.57(8H, m), 1.26(72H), 0.89(12H, t, J=6.6Hz)

<Example 35> Preparation of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate lauryl ether (pentaerythritol ethoxylate (15/4 EO/OH) laureth-10 carboxylate)

Except that 79.7 g (100 mmol) of pentaerythritol ethoxylate (15/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 7 was performed to obtain 286.3 g of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate lauryl ether (pentaerythritol ethoxylate (15/4 EO/OH) laureth-10 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.17(16H), 3.67(204H), 3.47(8H, t, $J=6.9\text{Hz}$), 1.57(8H, m), 1.28(72H), 0.88(12H, t, $J=6.6\text{Hz}$)

<Example 36> Preparation of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate cetyl ether (pentaerythritol ethoxylate (15/4 EO/OH) ceteth-4 carboxylate)

Except that 79.7 g (100 mmol) of pentaerythritol ethoxylate (15/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 8 was performed to obtain 199.3 g of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate cetyl ether (pentaerythritol ethoxylate (15/4 EO/OH) ceteth-4 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.17(16H), 3.66(108H), 3.47(8H, t, $J=6.6\text{Hz}$), 1.57(8H, m), 1.27(104H), 0.88(12H, t, $J=6.6\text{Hz}$)

<Example 37> Preparation of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate cetyl ether (pentaerythritol ethoxylate (15/4 EO/OH) ceteth-6 carboxylate)

Except that 79.7 g (100 mmol) of pentaerythritol ethoxylate (15/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 9 was performed to obtain 224.8 g of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate cetyl ether (pentaerythritol ethoxylate (15/4 EO/OH) ceteth-6 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.17(16H), 3.67(140H), 3.46(8H, t, $J=6.9\text{Hz}$), 1.56(8H, m), 1.26(104H), 0.87(12H, t, $J=6.6\text{Hz}$)

<Example 38> Preparation of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate cetyl ether (pentaerythritol ethoxylate (15/4 EO/OH) ceteth-10 carboxylate)

Except that 79.7 g (100 mmol) of pentaerythritol ethoxylate (15/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 10 was performed to obtain 301.2 g of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate cetyl ether (pentaerythritol ethoxylate (15/4 EO/OH) ceteth-10 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.18(16H), 3.67(204H), 3.47(8H, t, $J=6.9\text{Hz}$), 1.57(8H, m), 1.27(104H), 0.89(12H, t, $J=6.6\text{Hz}$)

<Example 39> Preparation of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate oleyl ether (pentaerythritol ethoxylate (15/4 EO/OH) oleth-6 carboxylate)

Except that 79.7 g (100 mmol) of pentaerythritol ethoxylate (15/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 11 was performed to obtain 290.4 g of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate oleyl ether (pentaerythritol ethoxylate (15/4 EO/OH) oleth-6 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 5.63(8H), 4.16(16H), 3.67(140H), 3.48(8H, t, $J=6.9\text{Hz}$), 2.02(16H), 1.57(8H, m), 1.27(80H), 0.87(12H, t, $J=6.6\text{Hz}$)

<Example 40> Preparation of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate stearyl ether (pentaerythritol ethoxylate (15/4 EO/OH) steareth-4 carboxylate)

Except that 79.7 g (100 mmol) of pentaerythritol ethoxylate (15/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 12 was performed to obtain 220.0 g of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate stearyl ether (pentaerythritol ethoxylate (15/4 EO/OH) steareth-4 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.17(16H), 3.68(108H), 3.47(8H, t, $J=6.9\text{Hz}$), 1.57(8H, m), 1.27(120H), 0.87(12H, t, $J=6.6\text{Hz}$)

<Example 41> Preparation of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate stearyl ether (pentaerythritol ethoxylate (15/4 EO/OH) steareth-6 carboxylate)

Except that 79.7 g (100 mmol) of pentaerythritol ethoxylate(15/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 13 was performed to obtain 241.3 g of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate stearyl ether (pentaerythritol ethoxylate (15/4 EO/OH) steareth-6 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.17(16H), 3.67(140H), 3.47(8H, t, $J=6.6\text{Hz}$), 1.57(8H, m), 1.27(120H), 0.87(12H, t, $J=6.6\text{Hz}$)

<Example 42> Preparation of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate stearyl ether (pentaerythritol ethoxylate (15/4 EO/OH) steareth-10 carboxylate)

Except that 79.7 g (100 mmol) of pentaerythritol ethoxylate (15/4 EO/OH) was used instead of pentaerythritol, the same procedure described in Example 14 was performed to obtain 300.7 g of pentaerythritol ethoxylate (15/4 EO/OH) glycolic ester ethoxylate stearyl ether (pentaerythritol ethoxylate (15/4 EO/OH) steareth-10 carboxylate).

$^1\text{H-NMR}$ (in CHCl_3): 4.17(16H), 3.67(204H), 3.47(8H, t, $J=6.9\text{Hz}$), 1.57(8H, m), 1.26(120H), 0.88(12H, t, $J=6.6\text{Hz}$)

<Experimental Example 1>Evaluation of the increase of moisture content in the skin

The degree of the increase of moisture content in the skin was measured for the compounds obtained in the Examples. The increase of moisture content in the

skin was measured by dividing 50 hairless Guinea pigs into 10 groups, and applying the compounds obtained in the Examples to each group.

Specifically, after the skin barrier was damaged by patching acetone using Finn chamber for 30 minutes to the flank site of the experiment animals, 200 μl of each experimental substance was applied to the patched site, then the moisture content of the stratum corneum of the site was measured using Corneometer and then evaluated. Apparatus measurements were carried out directly after and 6 hours, 12 hours, 24 hours and 48 hours after removing the acetone patch. Changes of moisture content in the skin were evaluated relative to the content measured directly after the acetone treatment, which was set to be 100. The results are shown in the following table 1.

[Table 1]

Compound		Directly after acetone treatment	After sample application			
			6 h	12 h	24 h	48 h
Vehicle (PG: EtOH =7: 3)		100	98	95	93	86
Glycerol		100	109	113	115	117
Example No.	5	100	98	99	103	105
	10	100	101	105	109	113
	17	100	103	106	108	104
	22	100	100	105	109	115
	29	100	106	109	111	109
	34	100	105	110	116	114
	38	100	108	111	112	114
	42	100	106	110	109	111

As shown in table 1, pentaerythritol derivatives of the present invention showed the effect of increasing moisture content inside the skin compared with

the vehicle (propylene glycol: ethanol = 7: 3), and showed a similar effect to glycerol.

<Experimental Example 2>Evaluation of moisture retaining ability in dry conditions

Moisture retaining ability was evaluated and compared for the compounds obtained in the Examples.

Specifically, samples were prepared such that the moisture content of the compounds obtained in the Examples was 60%, and while the samples were kept in a constant temperature and humidity chamber (18°C, RH 20%), the weight change of the samples was observed over time, thereby enabling evaluation of the changes in moisture content. The results are shown in the following table 2.

[Table 2]

Compound		Initial	1 h	2 h	4 h	6 h
Vehicle (PG: EtOH =7:3)		60	54	46	35	21
Glycerol		60	57	50	41	25
Example No.	5	60	58	55	49	41
	10	60	58	57	50	44
	17	60	57	53	47	38
	22	60	56	52	48	43
	29	60	57	55	50	43
	34	60	58	56	49	45
	38	60	58	52	44	29
	42	60	57	55	48	34

As shown in Table 2 above, pentaerythritol derivatives of the present invention showed high moisture retaining ability compared with the vehicle (propylene glycol: ethanol = 7: 3) and glycerol.

From the above results of Experimental Examples 1 and 2, it was found that pentaerythritol derivatives provided by the present invention are able to improve moisture retaining ability of the stratum corneum when applied to the skin, and especially they show high moisturizing ability even in dry conditions. Therefore, the cosmetic compositions comprising the pentaerythritol derivatives of the present invention provide long lasting moisture together with high moisturizing ability, and especially a high moisturizing effect even in dry conditions.

In the below Preparation Examples and Experimental Example 3, liquid crystal bases containing pentaerythritol derivatives of the present invention were prepared, to evaluate the stability of liquid crystal base.

<Preparation Examples 1~24> Preparation of liquid crystal base

Liquid crystal bases containing pentaerythritol derivatives obtained in the Examples were prepared. Liquid crystal bases were prepared by combining pentaerythritol derivative of the present invention, fatty acid and cholesterol in a proper composition on a basis of analytic condition of lipid. The type of fatty acids used and the content of each component are shown in the following table 3.

[Table 3]

Preparation Example	Pentaerythritol derivatives		Fatty acid		Cholesterol
	Type	Content	Type	Content	Content
1	Ex. 10	33.3	Stearic acid	33.3	33.3
2		33.3	Palmitic acid	33.3	33.3
3		39	Stearic acid	28	33
4		39	Palmitic acid	28	33
5		52	Stearic acid	16	32
6		52	Palmitic acid	16	32
7	Ex. 22	33.3	Stearic acid	33.3	33.3
8		33.3	Palmitic acid	33.3	33.3
9		39	Stearic acid	28	33
10		39	Palmitic acid	28	33
11		52	Stearic acid	16	32
12		52	Palmitic acid	16	32
13	Ex. 34	33.3	Stearic acid	33.3	33.3
14		33.3	Palmitic acid	33.3	33.3
15		39	Stearic acid	28	33
16		39	Palmitic acid	28	33
17		52	Stearic acid	16	32
18		52	Palmitic acid	16	32
19	Ex. 42	33.3	Stearic acid	33.3	33.3
20		33.3	Palmitic acid	33.3	33.3
21		39	Stearic acid	28	33
22		39	Palmitic acid	28	33
23		52	Stearic acid	16	32
24		52	Palmitic acid	16	32

<Experimental Example 3> Evaluation of the liquid crystal formability of liquid crystal base

Formation of non-formation of liquid crystal in the liquid crystal bases of

5 Preparation Examples 1~24 was evaluated using polarizing microscope. For most

compounds, polarizing results of the typical clover shape of lamella liquid crystal were observed. Figures 1 to 4 show the results.

From the above results, it was found that the pentaerythritol derivatives of the present invention can stably form liquid crystal inside a liquid crystal base.

5 The pentaerythritol derivatives of the present invention may be combined in the amount of 10~70% based on the total weight of liquid crystal base.

As described above, the pentaerythritol derivatives according to the present invention and the crystal base containing the same provide long lasting moisture together with high moisturizing ability, and especially a high moisturizing effect
10 even in dry conditions. Further, they may be usefully combined in skin moisturizing cosmetic compositions.

Hereinbefore, the present invention was illustrated through preferred embodiments, which may be varied by those skilled in the art within the extent of the technical spirit and scope of the present invention.